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14. ABSTRACT

We have used a suite of ten xerogel coatings to examine the surface response toward the settlement of fouling organisms in laboratory tests and in the field. The coatings are organically modified xerogel surfaces with tunable surface energy, hydrophobicity/hydrophilicity, and charge. Principle component analysis indicated the surface charge and hydrophobicity as expressed in the non-polar component of surface energy were the primary determinants of settlement responses. Quantitative analysis of genetics in settlement preference was begun and will be continued in future work.

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Final Technical Report for ONR N00014-13-1-0430

Materials Approach to Dissecting Surface Responses in the Attachment Stages of Biofouling Organisms

Michael R. Detty, PI/PD

Summary of Research Highlights Supported by ONR N00014-13-1-0430

1) Hydrophobic xerogel coatings are "robust" – good adhesion to glass, aluminum, fiberglass. Surfaces are highly reproducible.

2) The xerogel surfaces with uniform topography are good models for correlation of surface energy/critical surface tension/water contact angles/zeta potentials/charge with settlement of fouling organisms/materials and strength of adhesion of fouling organisms/materials.

3) Experimental xerogel surfaces incorporating trifluoropropyltrimethoxysilane (TFP), phenyltriethoxysilane (PH), carboxyethyltriethoxysilane (COE), *n*-octyltriethoxysilane (C8), *n*-octadecyltriethoxysilane (C18), aminopropyltriethoxysilanev(AP), dimethylaminopropyl-triethoxysilane (DMAP), and trimethylammoniumpropyltriethoxysilane (TMAP) were prepared to give xerogel formulations in the following molar ratios: 50:50 C8/TEOS, 5:45:50 C18/C8/TEOS, 20:80 TFP/TEOS, 50:50 TFP/TEOS, 20:80 PH/TEOS, 50:50 PH/TEOS, 10:90 AP/TEOS, 10:90 DMAP/TEOS, 10:90 TMAP/TEOS, and 10:90 COE/TEOS. These surfaces were used as standards in all biological assays

4) Five fouling organisms (barnacles, *Balanus Amphitrite* and *Balanus improvisus*, bryozoan *Bugula neritina*, oyster *Crassostrea gigas*, ascidian *Ciona intestinalis*) were tested in the laboratory for their settlement behavior in regards to the coating surfaces.

5) Multivariate statistical analysis was used to examine the effect (if any) of the experimental surfaces on attachment of biofouling organisms. Settlement behavior was found to be surface dependent. The barnacle *Balanus amphitrite* resulted in a settlement range of 3-34%, depending on the coating surface, after 24 hours. The barnacle *Balanus improvisus* resulted in a settlement range of 7-53%, depending on the coating surface, after 24 hours. The bryozoan, *Bugula neritina*, settled in a range of 20-80% depending on the coating surface after 30 minutes. The oyster, *Crassostrea giga*, produced a 0-7% settlement after 48 hours at 20˚C.

6) The 10 experimental coatings were applied to glass rods and were deployed in the field to evaluate settlement preferences. Canonical Analysis of Principal Coordinates were applied to results from field experiments – Although we have already determined that the attachment of biofouling organisms to coated glass rods in the field is affected by the coatings for all immersion durations up to 5 days, we have yet to determine which surface characteristics of the coatings caused these effects, and how those effects may (or may not) have changed over time. We will again use Canonical Analysis of Principal Coordinates to examine the influence of coating surface properties on the patterns in settlement observed in the field in the extension of this work over the coming year.

7) Quantitative genetic analysis of barnacle attachment – Treated glass were used to examine the settlement responses of 30 maternal families of barnacle larvae. Previous research has indicated that response of barnacle larvae to surfaces of differing surface energy varies across maternal families. Genetic correlations between responses to these surfaces suggest that at minimum 2 receptors are involved in generating the observed patterns. A subset of surfaces employed in the laboratory tests carried out previously were chosen for use, to represent a matrix of conditions of surface energy and surface charge. Patterns in genetic correlations will be analyzed in the extension of this work over the coming year with regard to these surface characteristics, using the

statistical approaches applied in the project's first year to develop a multidimensional (depending on the results of the assays) description of the barnacle attachment response.

Publications Citing ONR N00014-13-1-0430 for Support

1) Gatley, C. M.; Muller, L. M.; Lang, M. A.; Alberto, E. E.; Detty, M. R., Xerogel-Sequestered Silanated Organochalcogenide Catalysts for Bromination with Hydrogen Peroxide and Sodium Bromide. *Molecules*, **2015**, 20(6), 9616-9639.

2) Destino, Joel F.; Gatley, Caitlyn M.; Craft, Andrew K.; Detty, Michael R.; Bright, Frank V., Probing Nanoscale Chemical Segregation and Surface Properties of Antifouling Hybrid Xerogel Films. *Langmuir*, **2015**, 31(11), 3510-3517.

3) Damon, C. A.; Gatley, C. M.; Beres, J. J..; Finlay, J. A.; Franco, S. F.; Clare, A. S.; Detty, M. R. The Performance of Hybrid Titania/Silica-derived Xerogels as Active Antifouling/Fouling-release Surfaces against the Marine Alga *Ulva linza*: *in situ* Generation of Hypohalous Acids. *Biofouling* **2016**, submitted.

Patents Supported by ONR N00014-13-1-0430

1) Detty, M. R.; Damon, C. A.; Gatley, C. M. "Mixed Transition Metal Oxides Silica Xerogels as Antifouling/Fouling Release Surfaces," US Application 62/265,206 (December, 2015).

Invited Presentations Citing ONR N00014-13-1-0430 for Support

1) Detty, M. R. "Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling," Aquaculture 2013, Nashville, TN (Feb 25, 2013).

2) Detty, M. R. "Organically-modified Silicas as Anti-fouling/Fouling Release Coatings to Minimize Biofouling," Aquaculture 2016, Las Vegas, NV (Feb 23, 2016)..

Contributed Posters/Presentations Citing ONR N00014-13-1-0430 for Support (* denotes presenting author.)

1) Gatley, C.;* Holm, E.; Detty, M. R. "Multivariate Analysis of Attachment of Biofouling Larvae in Response to Material Surface Characteristics." Society for Integrative and Comparative Biology, West Palm Beach, FL (January, 2015).

2) Gatley, C.;* Holm, E.; Detty, M. R. "Multivariate Analysis of Attachment of Biofouling Larvae in Response to Material Surface Characteristics." 14th Pacific Polymer Conference, Poipu, HI (December, 2015).

Degrees Awarded Based on Research Supported by ONR N00014-13-1-0430

1) Dr. Caitlyn Gatley, University at Buffalo, Ph. D. in Medicinal Chemistry, December, 2016, Dissertation Title: *Multivariate Analysis of Attachment of Biofouling Larvae in Response to Material Surface Characteristics*.

Postdoctoral Associates Conducting Research Supported by ONR N00014-13-1-0430

None

Undergraduate Research Students (Two or More Semesters of Research Supported by ONR N00014-13-1-0430)

1) Mr. Joshua Beres, B. Sc. in Chemistry, May, 2017